Graphene on metals: a Van der Waals density functional study

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We use density functional theory (DFT) with a recently developed van der Waals density functional (vdW-DF) to study the adsorption of graphene on Al, Cu, Ag, Au, Pt, Pd, Co and Ni(111) surfaces. In constrast to the local density approximation (LDA) which predicts relatively strong binding for Ni,Co and Pd, the vdW-DF predicts weak binding for all metals and metal-graphene distances in the range 3.40-3.72 Å. At these distances the graphene bandstructure as calculated with DFT and the many-body G_0W_0 method is basically unaffected by the substrate, in particular there is no opening of a band gap at the K-point.

The recently reported synthesis of graphene[1], a single layer of graphite, ontop of a SiO_2 substrate has renewed the interest for this unique material. The uniqueness of this 2D crystal is mainly due to its very peculiar band structure, with the π and π^* bands showing linear dispersion around the Fermi level where they touch in a single point. The great variety of physics and chemistry which derives from this electronic structure makes graphene very attractive for a range of applications. In particular, its high stability and good conductivity under ambient conditions makes it an interesting candidate for future nano-scale electronics[2]. In this perspective, the interaction of graphene with metallic contacts plays a fundamental role. Moreover, catalytic growth of graphene on transition metal surfaces from carbon containing gases has become a standard way to obtain high quality graphene samples[3, 4, 5, 6]. Nevertheless the nature of the metal-graphene chemical bond is still not well understood.[3].

The widely used density functional theory (DFT) with local and semi-local functionals for exchange and correlation usually provides an accurate description of covalent and ionic chemical bonds. On the other hand it fails to reproduce non-local dispersive forces, in particular van der Waals forces, which are important in weakly bonded materials such as graphite, molecular crystals, and many organic compounds.[7, 8, 9]. It is also well known that the local density approximation (LDA) tends to overbind systems where van der Waals interactions are important, while the generalized gradient approximations (GGA) usually tend to underestimate the binding in these systems. In the case of graphene on metals many GGAs, contrary to experiments, predicts no binding at all, and therefore most theoretical work on graphene-metal interfaces has relied on the LDA. In view of the fact that LDA in general cannot be considered a reliable approximation in non-homogeneous systems such as surfaces and molecules, the graphene-metal interface clearly calls for new and improved functionals.

The interaction of graphene with the (111) surfaces of

Al, Cu, Ag, Au, Pt, Pd, Co and Ni was studied in Ref.[10] using the LDA approximation. The LDA results divide the metals into two classes: Co, Ni and Pd which bind graphene strongly and Al, Cu, Ag, Au and Pt which bind graphene weakly. In contrast PBE[12] gives no binding of graphene at room temperature[13]. This remarkable disagreement between the two most commonly used approximations of DFT might be related to the incorrect description of dispersion interactions in both of the functionals.

In this paper we use the recently developed van der Waals density functional (vdw-DF)[14, 15] to investigate the nature of the bonding at the metal-graphene interface. The functional is explicitly constructed to include non-local dispersion interactions and has proven successful in several cases where standard functionals fail, such as rare gases[14], benzene dimers[16, 17], graphite [18], polymers[19], DNA[20] and organic molecules on surfaces[21, 22, 23]. Within the vdw-DF approximation, the exchange-correlation energy is

$$E_{xc}^{\mathrm{vdw-DF}} = E_x^{\mathrm{revPBE}} + E_c^{\mathrm{LDA}} + E_c^{\mathrm{nl}} \qquad (1)$$

where E_x^{revPBE} is the revPBE[11] exchange energy, E_c^{LDA} is the LDA correlation energy and E_c^{nl} is the non-local correction given by

$$E_c^{\mathrm{nl}} = \frac{1}{2} \iint n(\mathbf{r_1})n(\mathbf{r_2})\phi(q_1,q_2,r_{12})\mathrm{d}\mathbf{r_1}\mathrm{d}\mathbf{r_2} \qquad (2)$$

where $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$ and q_1 and q_2 are values of a universal function $q_0(n(\mathbf{r}), |\nabla n(\mathbf{r})|)$. Eq. (2) is efficiently evaluated by factorizing the integration kernel ϕ and by using fast Fourier transform to compute the selfconsistent potential as proposed in Ref. [24] and implemented in the real-space projector augmented wave GPAW code[30].

In this study we consider Al, Cu, Ag, Au, Pt, Ni, Co and Pd metal (111) surfaces. We fix the atoms in the metal slabs at their experimental lattice parameters and relax the graphene sheet using the vdw-DF Hellmann-Feynman forces. We use a (6,6,1) and (4,4,1) Monkhorst Pack k-point sampling respectively for the smaller (Ni,

		Al	Cu	Ag	Au	Ni	Co	Pt	Pd
vdw-DF	d (Å)	3.72	3.58	3.55	3.57	3.50	3.40	3.67	3.50
	E_b (meV)	35	38	33	38	37	30	43	39
	ΔE_{F} (eV)	-0.51	-0.43	-0.40	+0.21	+0.13	-0.20	+0.66	+0.65
	δQ ($10^{-3}e$)	-8.0	-4.0	-5.0	+0.4	-3.0	-5.0	+5.0	+0.5
LDA	d (Å)	3.46	3.21	3.32	3.35	2.08	2.08	3.25	2.33
	E_b (meV)	25	35	45	31	123	175	33	79
revPBE	d (Å)	-	-	-	-	-	-	-	-
	E_b (meV)	-	-	-	-	-	-	-	-

TABLE I: Binding energies (E_b) per carbon atom and binding distances (d) of graphene on metal (111) surfaces; '-' means no binding. Fermi level shift ΔE_{F} and charge transfer δQ of graphene adsorbed on the different metals at the vdw-DF equilibrium separation. Negative (positive) ΔE_{F} indicates n (p)-type doping. Negative (positive) δQ indicates electron transfer to (from) the graphene layer. The charge transfer has been evaluated according to the Bader scheme[31].

FIG. 1: Binding energy (E_b) per carbon atom of graphene on the Ni(111) surface calculated with LDA, revPBE and vdw-DF functionals. The graphene is adsorbed in the top-fcc configuration.

Cu, Co) and the larger (Au, Ag, Pt, Pd, Al) orthorombic unit cells. The metal slabs are modeled with 4 atomic layers and a vacuum of 14 Å in the direction normal to the surface; the grid spacing is 0.16 Å. The calculated binding energies and distances for the relaxed structures are listed in Table I. The vdW-DF results show that the metal-graphene interaction is relatively similar across the different metals. This is in contrast with the LDA prediction of two separate classes of metal-graphene interfaces, as found in very good agreement with [10]. We also repeated the same calculations using the revPBE functional and we obtained no binding for any of the metals. Interestingly, for the systems that LDA finds to be weakly bonded (Al, Cu, Ag, Au and Pt), the binding energies obtained with the vdw-DF are very similar to the LDA ones. Nevertheless the binding distances are systematically slightly larger in the vdw-DF case. In fact it has been reported that the vdw-DF functional usually produces equilibrium distances somewhat larger than experiments[21]. In the case of Ni, Co and Pd, on the other hand, the relatively strong binding predicted by LDA is not found by the vdw-DF functional.

In order to analyze these results, we now focus on the interaction between graphene and Ni(111). Fig. 1 shows the binding curves for graphene on the Ni(111) surface calculated with the LDA, revPBE and vdw-DF functionals. The revPBE curve is positive at all distances, while the LDA curve shows a relatively deep minimum at ~ 2 Å consistent with previous LDA calculations. The vdw-DF result lies in between, following the revPBE curve at small separations and the LDA curve at larger separations, and it predicts a shallow minimum at 3.5 Å. Note that a local minimum is found by the revPBE functional around 2 Å.

In Fig. 2 we show the calculated bandstructure of graphene on Ni(111). The color of the dots indicate the weight of the corresponding Bloch eigenstate on the c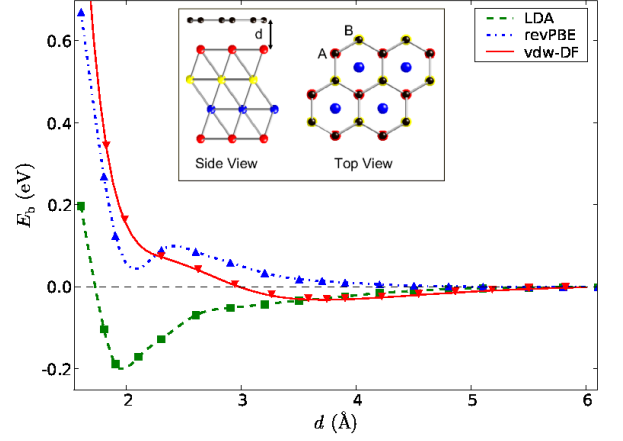arbon p_z orbitals with darker meaning larger weight. In free graphene, the carbon p_z orbitals placed at A sites (p_z^{A}) are decoupled from the p_z orbitals at B sites (p_z^{B}) at the Dirac point, thus producing two degenerate states (see inset in Fig. 1 for the structure). Since the A sites are located directly on top of Ni atoms at a close distance in the LDA calculation (2.08 Å), a strong hybridization between p_z^{A} orbitals and $\mathrm{Ni}_{3z^2-r^2}$ is observed, which gives rise to an unoccupied antibonding state σ^* and two occupied bonding states σ_1 and σ_2. The LDA gaps for $\sigma^*-\sigma_1$ and $\sigma^*-\sigma_2$ are 2 eV and 4 eV, respectively. On the other hand, the p_z^{B} orbitals (occupied in the spin up channel and unoccupied in the spin down one) hardly interact with Ni d states and therefore remain unmodified. The vdw-DF band structures (evaluated at the vdw-DF relaxed distance of 3.50 Å), on the other hand, resemble the free graphene, preserving the Dirac point and only shifting it up by 0.13 eV. A very similar behaviour is found for Co and Pd. For the remaining interfaces both the LDA and vdw-DF bandstructures resemble that of free standing graphene with the Dirac point shifted with respect to the metal Fermi level. The Fermi level shifts and calculated charge transfer between the metal and graphene are summarized in Table I.

Since LDA is known to underestimate band gaps significantly we have also performed $\mathrm{G}_0\mathrm{W}_0$ calculations for the graphene-Ni structures corresponding to the LDA and vdw-DF distances.[25] In both cases we find no noteworthy difference between the $\mathrm{G}_0\mathrm{W}_0$ and DFT Kohn-Sham band structures close to the K-point.

Recent experimental work on the graphene/Ni interface is based on Angle Resolved Photoemission Spectroscopy (ARPES). The ARPES band structures reveal a band gap at the graphene K-point thus suggesting some hybridization between the graphene and Ni orbitals[27, 28]. Earlier LEED measurements found a
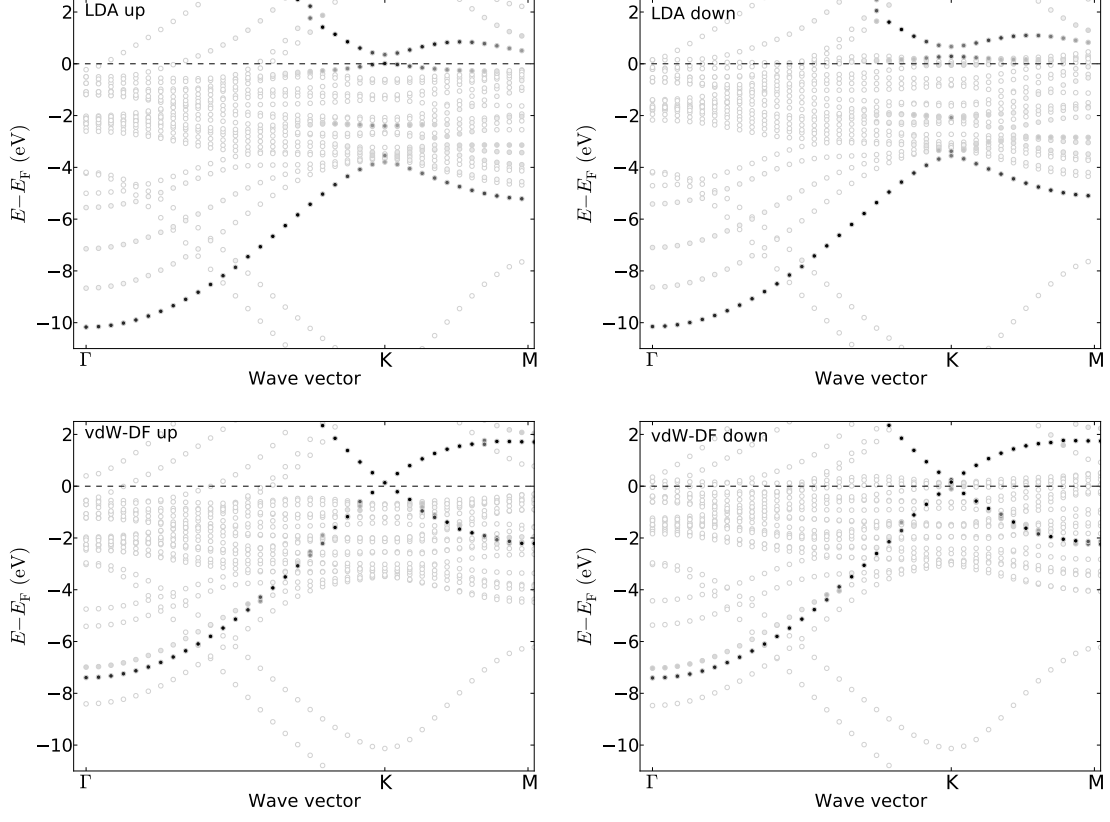
Graphene on Ni(111)

FIG. 2: LDA (top) and vdw-DF (bottom) spin polarized band structures for graphene on Ni(111) in the top-fcc configuration. Darker dots represent larger weight of the carbon p_z orbitals.
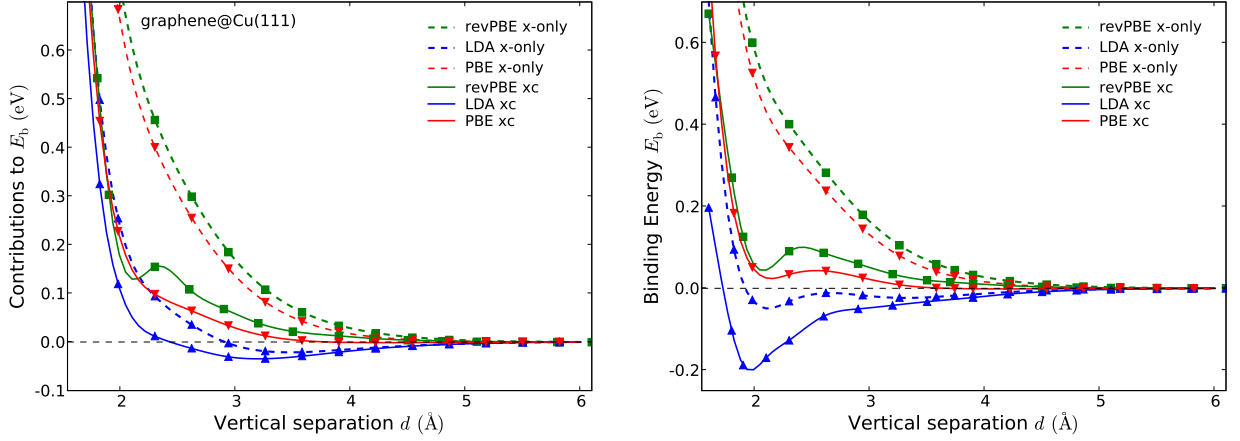

FIG. 3: Decomposition of the binding energy E_b into exchange-only contributions (dashed lines - only the correlation term is removed) and total binding energy (full lines) for different functionals.

Ni-graphene bond distance of 2.1Å[29]. We note that both of these results are in line with the LDA calculations. On the other hand LDA is not expected to work well for highly inhomogeneous systems such as the interface structures investigated here. These results indicate

a difficulty for the present vdw-DF in describing systems with mixed bonding character, in line with the conclusions of [23].

Fig. 3 shows the total (full lines) and the exchange-only (dashed lines) binding energy curves for revPBE,

PBE and LDA in the case of graphene on Cu(111) (left panel) and on Ni(111) (right panel). The exchange-only energies are calculated without including the correlation energy term in the exchange-correlation functional and have been evaluated non selfconsistently. Clearly, the bonding for the physisorbed graphene on Al, Cu, Ag, Au and Pt originates partially from the exchange term in the LDA xc-functional, as shown for Cu as an example in the left panel of Fig. 3 . This is in principle incorrect since van der Waals interactions are purely non-local correlation effects. The weak bonding predicted by the vdw-DF functional, similar in magnitude to the LDA results, is produced by the correlation term instead, which is physically correct. Interestingly, this applies to the Ni/graphene system as well, as shown in the right panel of Fig. 3.. The LDA exchange-only curve shows a broad and weak attractive contribution between 2 Å and 5 Å with two local minima. We note that in a genuine covalent bond the exchange contribution to the binding energy is generally significantly larger than in this case. The revPBE and PBE exchange-only curves are repulsive at all separations for both systems. This is the typical behaviour which is observed in van der Waals bonded dimers or organic molecules on surfaces[14, 22]

In conclusion we have performed DFT calculations of graphene adsorbed on different metal surfaces using the recently developed vdw-DF functional which explicitly includes non-local correlations. For Al, Cu, Ag, Au and Pt both LDA and vdw-DF consistently predicts a weak binding. Similar weak binding is found for Ni, Co and Pd with the vdw-DF where LDA on the other hand predicts stronger binding and significant hybridization between graphene and metal d-states. At the vdw-DF binding distances graphene's band structure was shown to be essentially unaffected by the substrate. This appears to be in conflict with LEED and ARPES measurements for graphene on Ni, indicating that more work is needed in order to reconcile experiments and theory for the graphene-metal interface.

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